Ion-Beam Induced Nano-Sized Ag Metal-Clusters in Glass

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Abstract

Silver metal clusters have been formed in soda lime glass by high-energy heavy ion irradiation at ISL. The metal cluster formation was detected with X-ray absorption spectroscopy (EXAFS) in fluorescence mode, and the shape of the clusters was imaged with transmission electron microscopy. While annealing in reducing atmosphere alone already leads to the formation of metal clusters in Ag containing glasses, where the Ag was introduced by ion-exchange, such clusters are not very uniform in size and are randomly distributed over the Ag-containing glass volume. Irradiation with 600-MeV Au ions followed by annealing, however, results in clusters more uniform in size and arranged in chains parallel to the direction of the ion beam.

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1. Introduction

Glasses containing metal clusters have attracted quite some attention both in cluster research and in possible applications of such clusters for magnetic or optoelectronic purposes. So exhibit nanometer-sized clusters of noble metals in glasses strong absorption of visible light which, in addition, may be highly polarization dependant depending on size and shape with special alignment of the clusters [1, 2]. Various preparation methods are pursued to obtain control of the mechanisms to form such clusters. A promising approach is the irradiation of glasses containing the wanted metal as a metal oxide with heavy-ion beams at MeV energies. This procedure has been investigated in the case of soda lime glass with Cu clusters from Cu_2O in the original mixture of the oxides [3] and with Ag clusters from the incorporation by ion-exchange [4, 5]. In both cases metal clusters were already produced by other means of treatment, such as heat-treatment in reducing atmosphere and/or laser irradiation. By using ion beams, it could be shown that the special energy deposition due to the electronic stopping of heavy ions may be advantageous to the cluster size distribution (see the detailed discussion in ref. [3]). Furthermore, irradiation with ion beams with considerable electronic stopping power results in alignment effects of the clusters along the ion beam direction. This was demonstrated by 30-MeV Si ion irradiation of Ag clusters, which were nucleated with 1-MeV Xe irradiation at high fluences [5]. Similarly, modification of size and shape (elongation) have been observed for Co nanoparticles in SiO_2 by 200-MeV ^{127}I ion irradiation [6]. These studies prompted us to investigate metal cluster formation in glasses with ions of very high electronic stopping power with the possibility of forming metal wires along the ion tracks, hundreds of nanometer, up to micrometers long with diameters of the typical size of an ion track of some nm.

Access to the understanding of the cluster formation can be obtained by methods sensitive to the local structure which is not obscured when only nanometer-sized objects are investigated. Such a technique is provided by the extended X-ray absorption fine structure (EXAFS) [7] which we employed to follow the transformation from the oxide coordination to the metal cluster. For information on the shape of the metal clusters we used transmission electron microscopy (TEM) and have started experiments with small angle X-ray scattering.

2. Experimental

We have used the ion-exchange process to incorporate Ag into borosilicate glass. Glass plates, 0.1 or 0.15 mm thick, were immersed in a molten salt bath of a mixture of 1% mol $AgNO_3$ and $NaNO_3$ at a temperature of 340 °C for 30 min. The samples were mounted, self-supporting in Cu-frames, onto a cold Cu plate kept at LN_2 temperature and irradiated with 600-MeV Au ions from the ISL accelerator facility with fluences of 1 x 10^{11} to 1 x 10^{13} ions/cm^2. The ion flux was kept below 10^{10} ions/cm^{2}s. The same fluence was applied onto both sides of the plates since the projected range is approximately only half the thickness of the glass plates. The plates were only loosely mounted in order to allow for expected ion beam induced plastic deformation. For a better thermal contact a thin Au layer of 10 μg/cm^2 was evaporated onto the surface, and the glasses were fixed to the Cu frames with conductive carbon glue at the edges. In spite of these preventive measures, some of the samples, irradiated with the higher fluences, developed cracks.

Following the ion irradiation, the samples were investigated with X-ray absorption spectroscopy at the Ag K-edge (25.514 keV) either with or without further annealing at the same temperature as for the ion-exchange preparation under a reducing atmosphere (5% H_2-Ar mixture) for 30 min (see ref. [4]). The EXAFS experiment was performed at the X1 beamline of HASYLAB with the

samples kept close to LN_2 temperature. The absorption was measured in fluorescence mode using a 7-element Ge detector. For comparison, the absorption was measured for samples of Ag metal and a sample of Ag_2O powder, mixed with graphite and polyethylene and pressed into a pill, too. The EXAFS spectra were analysed using the standard FEFF procedures [8, 9, 10] by which the coordination numbers and distances at least for the first and second coordination shells could be derived.

For transmission electron microscopy (TEM) thin slices of some 10 nm were cut out of the samples parallel to the ion impact and deposed onto a fine grid. The TEM was operated at 120 kV.

Results and discussion

An example of the EXAFS spectra is presented in Fig.1. It illustrates the transformation from Ag oxide into Ag metal. The distances to the first and second coordination shells around the central Ag atom as determined by the EXAFS analysis are summarized in Table1. The bond length of Ag to O in the glass is slightly larger than in pure Ag_2O. This difference may reflect the substitution of Na by Ag as an impurity, for Ag_2O in glass the bond length is known to be $d_{Na\text{-}O}$= 2.32 Å.

However, even in the situation shown, the transformation into Ag metal is not complete. Approximately 30 % of the Ag is surrounded by Ag, while the major part of Ag atoms is ambiented by oxygen. With no post-irradiation heat treatment the metal fraction is at the detection limit. Obviously, the metal fraction strongly depends on the treatment following the ion irradiation.

Since EXAFS provides practically no shape and only very crude size information we have complemented the study with transmission electron microscopy. In Fig.2 we present a comparison of TEM images for a non-irradiated sample and a sample exposed to a fluence of 1×10^{12} ions/cm^2. Both specimens were annealed at 340°C for 30 min in reducing atmosphere showing the signifi-

cant influence of the ion irradiation: (i) the metal clusters have grown and their size distribution has become more uniform, but the most remarkable feature is that (ii) the clusters are arranged in chains parallel to the direction of the ion beam. Since some of the chains consist of clusters very similar in diameter and almost in contact, one is tempted to speculate that a totally columnar structure may be obtained by controlling the influencing parameters such as the ion fluence and the annealing parameters.

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Table 1

Distances in the first and second coordination shell for Ag in glass, metal and oxide as determined by EXAFS (all values in Å).

System	1.Shell	2.Shell
Ag in glass	2.85(2) 2.25(10)	
Ag metal	2.87(1) 2.889*	4.06(3) 4.085*
Ag_2O	2.05(2) 2.05*	3.26(4) 3.33*

* values from the standard lattice parameters

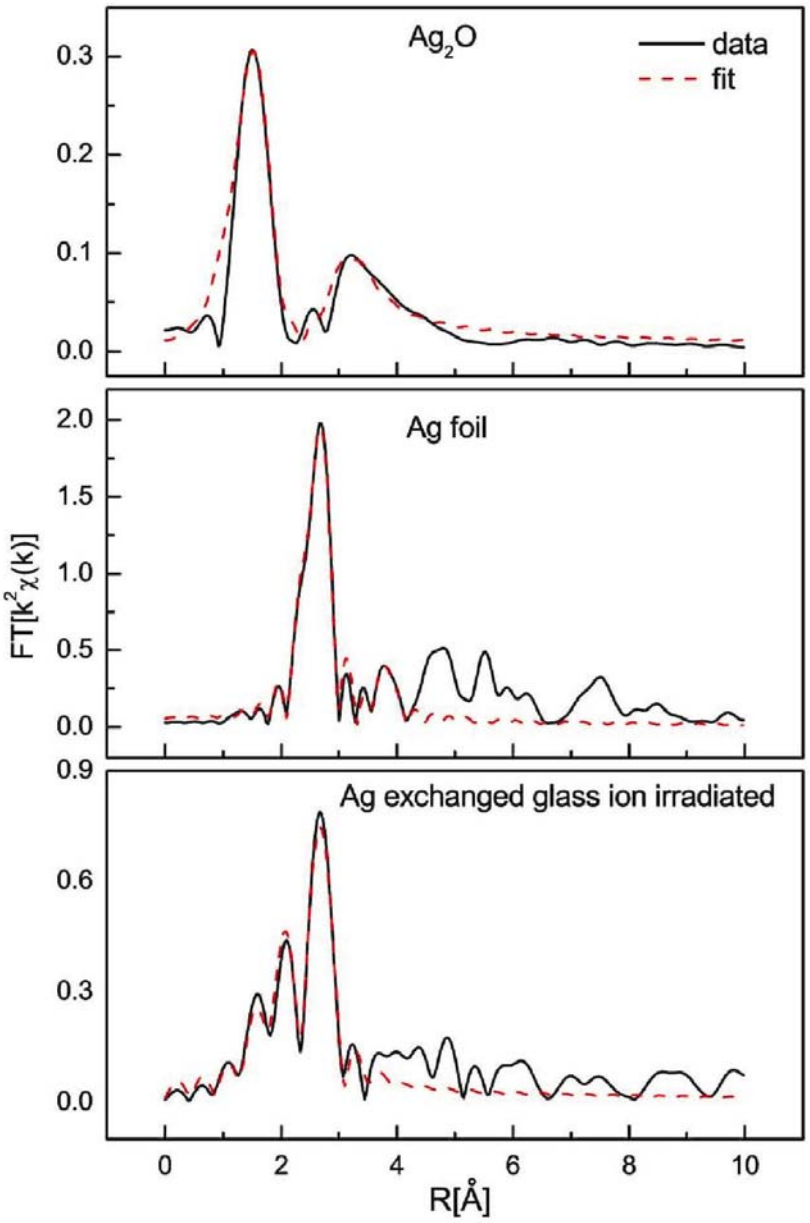

Fig. 1: Radial distribution function (Fourier transform) of the k^2-weighted EXAFS spectrum of the Ag exchanged glass, ion irradiated and annealed in reducing atmosphere, (bottom) compared with spectra for a Ag metal foil (center) and for Ag_2O (top).

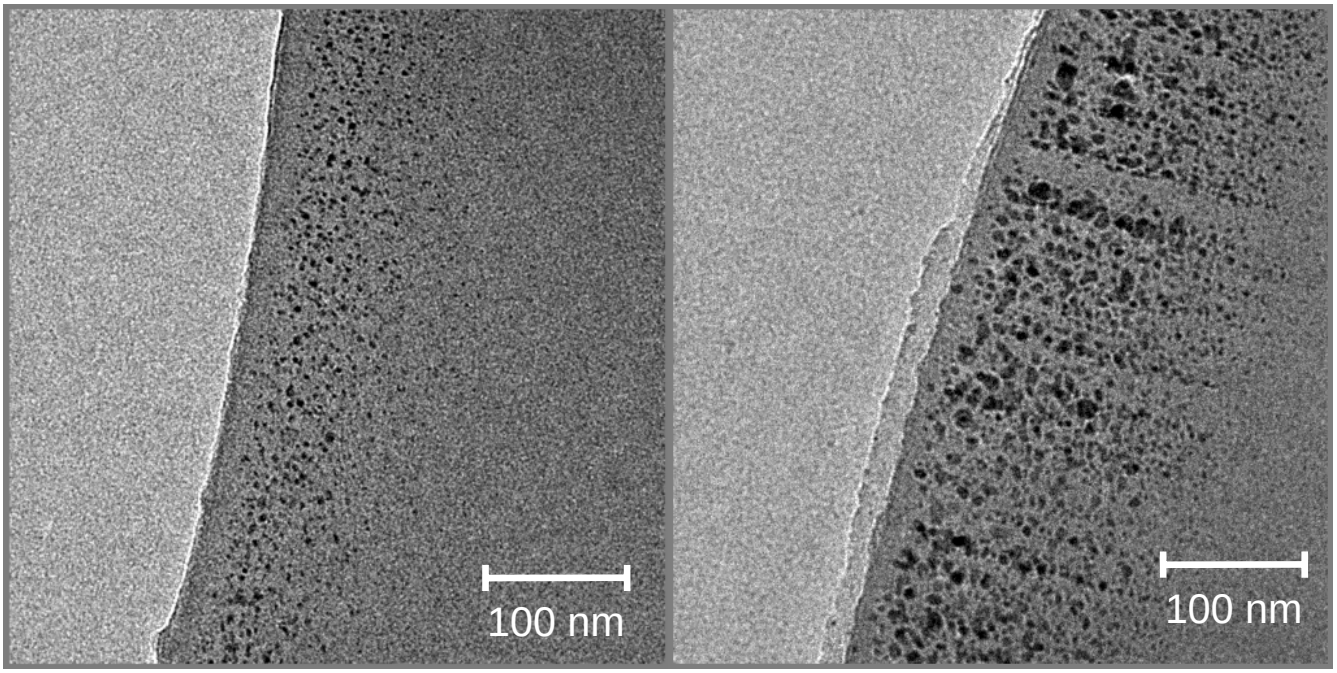

Fig. 2: TEM images of Ag ion exchanged glass, annealed only (left) and Au ion irradiated and subsequently annealed for 30 min at 340 °C (right), the surface being at the left side.